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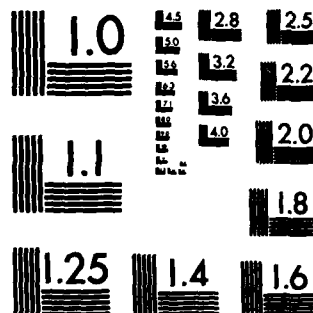
TWO CONDUCTING STACKED-RING POLYMERS: IODINE-DOPED
POLY(FLUOROALUMINUM 23. (U) CASE WESTERN RESERVE UNIV
CLEVELAND OHIO DEPT OF CHEMISTRY L A SCHECHTMAN ET AL.
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Two Conducting Stacked-Ring Polymers: Iodine-Doped Poly(Fluoroaluminum
2,3-Naphthalocyanine) and Iodine-Doped Poly(Fluorogallium 2,3-Naphthalocyanine)

by

Lee A. Schechtman and Malcolm E. Kenney

Paper Presented at

Electrochemical Society Meeting
San Francisco, CA
May 9, 1983

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TWO CONDUCTING, STACKED-RING POLYMERS: IODINE-DOPED POLY(FLUOROALUMINUM 2,3-NAPHTHALOCYANINE) AND IODINE-DOPED POLY(FLUOROGALLIUM 2,3-NAPHTHALOCYANINE)

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Work done by Curry and Cassidy (1) more than twenty years ago showed that halogen-doped copper phthalocyanines have conductivities which are much higher than the conductivity of copper phthalocyanine itself. Over the past few years work done on a number of other doped metal phthalocyanines has shown that many of them also have higher conductivities than do their parents.

Some of the doped species which are highly conducting are stacked-ring, polymeric phthalocyanines, e.g., iodine-doped poly(fluoroaluminum phthalocyanine). This has led us to a study of iodine-doped poly(fluoroaluminum 2,3-naphthalocyanine) and iodine-doped poly(fluorogallium 2,3-naphthalocyanine). Of necessity this required us to study the parent polymers, Figure. 1.

The routes used to make the parent polymers are based in part on earlier work by Linstead (2) and Luk'yanets (3). The initial compound prepared in the synthesis of fluoroaluminum naphthalocyanine was 2,3-naphthalenedicarbonitrile. This was made by reacting $\alpha,\alpha,\alpha',\alpha'$ -tetra-bromo-o-xylene with fumaronitrile and sodium iodide in dimethylformamide. It was converted to chloroaluminum naphthalocyanine by treating it with aluminum chloride in quinoline. The chloride thus obtained was hydrolyzed to the hydroxide by stepwise treatment with sulfuric acid and ammonium

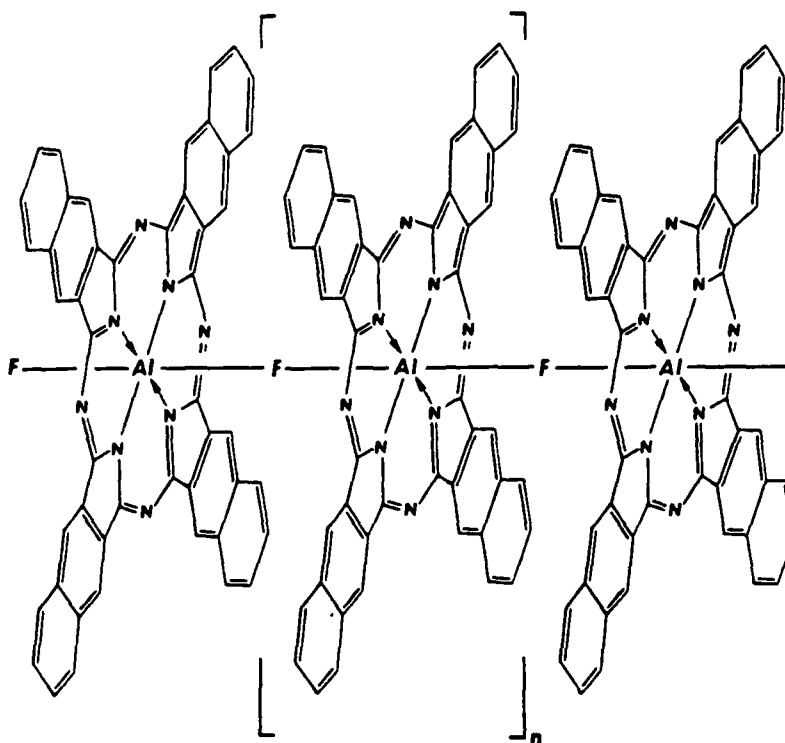


Figure 1

hydroxide. In turn, the hydroxide was converted to the tri-n-hexylsiloxide by reacting it with chloro-tri-n-hexylsilane in pyridine. The siloxide was recrystallized and then treated with hydrofluoric acid. Finally the fluorinated product was heated under vacuum. To buttress this work, pure samples of each of the intermediates were made, and the identities of these and of the fluoride were verified by elemental analysis.

The gallium fluoride was made in a generally similar way except that tri-n-hexylsilanol was used to prepare the siloxide intermediate. In separate work, each of the macrocyclic intermediates was prepared in pure form. The identities of these intermediates and of the fluoride were verified by elemental analysis.

As expected, the fluorides are green when finely divided. They are stable to handling and storage. They are also stable at 500° under vacuum, but they do not sublime perceptibly under these conditions. The two polymers give infrared spectra of the expected kind. The aluminum polymer yields an X-ray powder pattern indicating a ring-ring spacing of 3.54Å while the gallium polymer yields a powder pattern indicating a spacing of 3.69Å. It is presumed that the metal-fluorine backbones of the polymers are, like that of poly(fluorogallium phthalocyanine), linear.

The doped polymers were prepared by treating their parent polymers with iodine-pentane solutions. When lightly to moderately doped polymers were being made, the doping reaction went very readily.

The doped polymers give infrared spectra that show strong electronic excitation absorptions and Raman spectra that indicate the presence of I_3^- and I_5^- ions. The polymers, when highly doped and finely divided, are black.

For the conductivity studies, samples of the parent polymers and of the doped polymers having various iodine contents were made and pressed into disks. A combination of elemental analysis and thermogravimetric analysis was employed to determine the iodine contents of the doped polymers. The conductivities of the disks were determined by the linear four point probe technique.

The highest conductivity found for the doped aluminum polymer was 1.4S/cm. This was found in a sample having an iodide/ring ratio of 1.6. In the case of the doped gallium polymer, the highest conductivity found was 1.0S/cm. This occurred in a sample with the same iodine/ring ratio, 1.6.



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At low to moderate doping levels the conductivities of both doped polymers increase with doping level. At comparable doping levels the aluminum polymer has a higher conductivity than does the gallium polymer. The conductivities of both polymers at low to moderate doping levels are larger than those of their phthalocyanine analogs. Disks of the doped polymers are stable to handling and storage.

It appears likely that these doped polymers contain both cationic and neutral chains. The charge distribution along the charged chains could well be non-uniform. In accordance with earlier conclusions about polymers of this type, it is assumed that the rings of the charged chains bear fractional charges and that the conducting pathways are of the ring-ring type.

On the basis of the data gathered, it appears that the conductivities of these polymers are inversely proportional to their ring-ring separations. Further, it seems probable that the large size of the rings in them underlie in part the high conductivities they have. Whether or not the rings are eclipsed and, if so, what influence this has on their conductivities is unknown.

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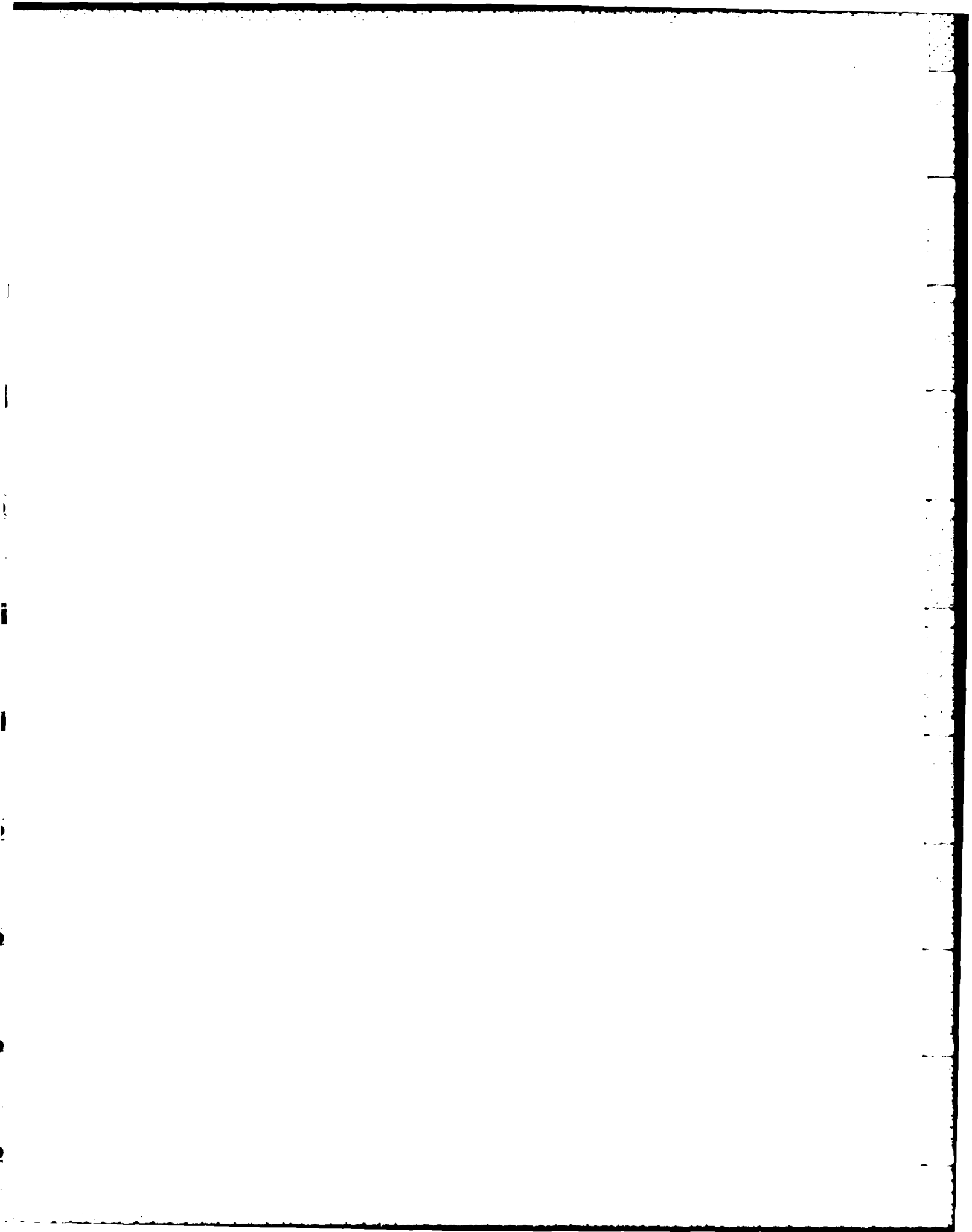
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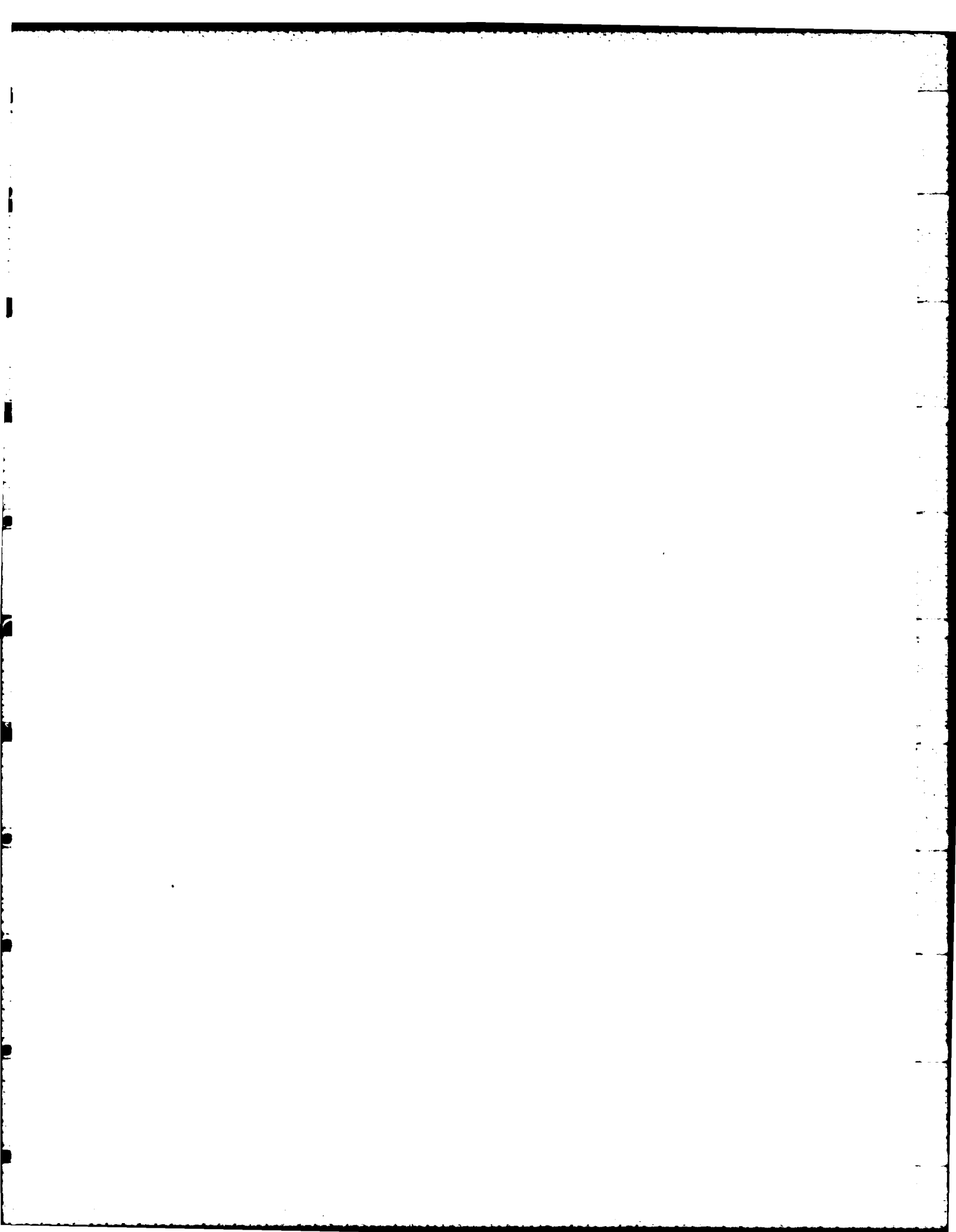
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